

**IONIC LIQUIDS FOR HETEROGENISING METALLOCENE CATALYSTS.**

- 5     The present invention relates to the use of ionic liquids to heterogenise metallocene catalyst components and thus prepare catalyst systems that are very active for the polymerisation of olefins.

10     Ionic liquids have been described in literature such as for example in US -A- 5,994,602, or in WO96/18459 or in WO01/81353. They disclose various methods for preparing ionic liquids and various applications.

15     These applications comprise oligomerisation of ethene, propene or butene with various nickel-based precursors dissolved in ionic liquids as disclosed for example in Dupont et al. (Dupont, J., de Souza R.F., Suarez P.A.Z., in Chem. Rev., 102, 3667, 2002.). The same document also discloses that Ziegler -Natta type polymerisation can be carried out in dialkylimidazolium halides/ammonium halide ionic liquids using  $AlCl_{3-x}R_x$  as cocatalysts.

20     Other applications include the use of ionic liquids that are liquid at or below room temperature as solvents for transition-metal-mediated catalysis, such as described for example in Welton (Welton T., in Chem. Rev., 99, 2071, 1999.). Most attempts have proven successful in dimerisation or oligomerisation, but polymerisation remains problematic, especially with metallocene catalyst  
25     components.

30     There is thus a need to develop new metallocene catalyst systems heterogenised by ionic liquids that are active in the polymerisation of  $\alpha$  - olefins.

It is an aim of the present invention to provide a method for preparing a metallocene catalyst component heterogenised by an ionic liquid.

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It is a further aim of the present invention to provide a process for polymerising alpha-olefins using a metallocene catalyst component heterogenised by an ionic liquid.

It is also an aim of the present invention to prepare new polymers with said new catalyst system.

Accordingly, the present invention discloses a method for preparing an heterogenised metallocene catalyst component for the polymerisation of alpha-olefins that comprises the steps of:

- a) providing a halogenated precursor component of formula (I)



- b) reacting the halogenated precursor with an ionic liquid precursor in a solvent to prepare an ionic liquid;



- c) optionally, reacting the intermediate  $\text{IL}^+\text{X}^-$  with a salt  $\text{C}^+\text{A}^-$ , wherein  $\text{C}^+$  is a cation that can be selected from  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ , and  $\text{A}^-$  is an anion that can be selected from  $\text{PF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{BF}_4^-$ ,  $(\text{CF}_3\text{—SO}_2)_2\text{N}^-$ ,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{NO}_3^-$  or  $\text{CF}_3\text{CO}_2^-$ .

- d) using the ionic liquid obtained in step b) or c) to heterogenise a complex of formula (II)



- wherein Cp and C'p are independently selected from substituted or unsubstituted cyclopentadienyl groups M is a metal selected from Group 4 of the Periodic Table, R'' is a structural bridge imparting stereorigidity between Cp and Cp' and Q is a halogen or an alkyl having from 1 to 12 carbon atoms and wherein the amounts of ionic liquid and catalyst components are in a molar ratio (ionic liquid)/(catalyst component) of from 5:1 to 1:5;
- e) heterogenising the ionic liquid /metal system by addition of an apolar solvent inducing the precipitation reaction;
- f) retrieving a metallocene catalyst component heterogenised by an ionic liquid.

Preferably, the ionic liquid and catalyst components are in stoichiometric amounts.

The groups  $(CpR^m)$  and  $(Cp'R^n)$  may include substituted or unsubstituted indenyl or fluorenyl groups. The position and nature of the substituents  $R^m$  and  $R^n$  is not particularly limited.

Preferably, the metallocene catalyst component is a bis-indenyl, a bis-benzindenyl or a bis-tetrahydroindenyl, substituted or unsubstituted.

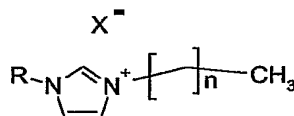
Particularly suitable metallocene catalyst components can be selected from ethylene bis-tetrahydroindenyl zirconium dichloride, or dimethylsilyl bis(2-Me-benzindenyl) zirconium dichloride or dimethylsilyl bis(2-Me-4-Ph-indenyl) zirconium dichloride.

All reactions are carried under argon at atmospheric pressure, using the standard Schlenk or glovebox techniques.

In the ionic liquid, the anion  $X^-$  can be selected from  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $SbF_6^-$ ,  $NO_2^-$  and  $NO_3^-$ . It can also be selected from compounds of formula  $AlR_{4-z}A''_z$  wherein R can be selected from an alkyl having from 1 to 12 carbon atoms, substituted or unsubstituted, or from a cycloalkyl having 5 or 6 carbon atoms, substituted or unsubstituted, or from an heteroalkyl, substituted or unsubstituted, or from an heterocycloalkyl, substituted or unsubstituted, or from an aryl having 5 or 6 carbon atoms, substituted or unsubstituted, or from an heteroaryl, substituted or unsubstituted, or from an alkoxy, an aryloxy, an acyl, a silyl, a boryl, a phosphino, an amino, a thio or a seleno, wherein  $A''$  is a halogen and wherein z is an integer from 0 to 4. The cationic part of the ionic liquid may be prepared by protonation or alkylation of a compound selected from imidazole, pyrazoline, thiazole, triazole, pyrrole, indone, tetrazole, pyridine, pyrimidine, pyrazine, pyridazine, piperazine or piperidine.

Preferably, the anion  $X^-$  is  $Br^-$  or  $BF_4^-$ , and preferably the cationic part is derived from imidazolium or pyridinium.

If the ionic liquid precursor is N-alkyl-imidazolium, the reaction is carried out at a temperature of from 50 to 150 °C, preferably of from 80 to 120 °C and for a period of time of from 1 to 24 hours, preferably of from 2 to 6 hours. The resulting intermediate product is an ion pair of formula III

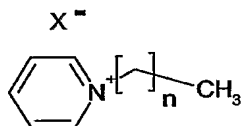


(III)

If the ionic liquid precursor is pyridinium, the reaction is carried out at a temperature of from 50 to 120 °C, preferably of from 90 to 110 °C and for a

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period of time of from 1 to 24 hours, preferably of about 2 hours. The resulting product is an ion pair of formula IV

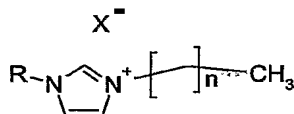


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(IV)

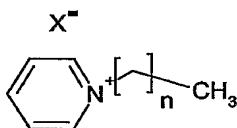
The intermediate products III or IV are then mixed with a complex of formula  $\text{R}''$  ( $\text{CpR}^m$ ) ( $\text{Cp}'\text{R}^n$ )  $\text{M Q}_2$  in a solvent selected typically from  $\text{CH}_2\text{Cl}_2$ , THF, or toluene, at room temperature (about  $25^\circ\text{C}$ ), for a period of time of from 1 to 24 hours, preferably of from 1 to 2 hours. After evaporation, the resulting product is precipitated in an apolar solvent to give a catalytic component of formula V if the ionic liquid precursor is a N-alkyl-imidazolium

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 $\text{R}''$  ( $\text{CpR}^m$ ) ( $\text{Cp}'\text{R}^n$ )  $\text{M Q}_2$ 

(V)

or of formula VI if the ionic liquid is pyridinium

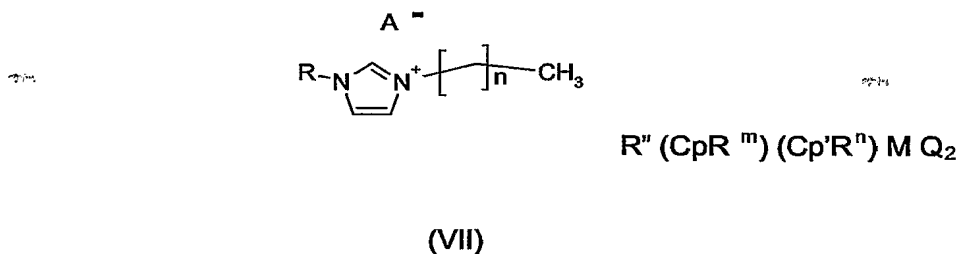
 $\text{R}''$  ( $\text{CpR}^m$ ) ( $\text{Cp}'\text{R}^n$ )  $\text{M Q}_2$ 

(VI)

The apolar solvent is selected in order to induce precipitation of the catalyst component: it can be heptane for example.

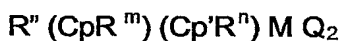
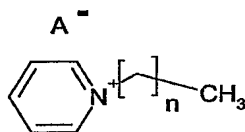
- 5 Optionally, the intermediate product (III) or (IV) can be reacted with a salt  $C^+A^-$ , wherein  $C^+$  is a cation that can be selected from  $K^+$ ,  $Na^+$ ,  $NH_4^+$ , and  $A^-$  is an anion that can be selected from  $PF_6^-$ ,  $SbF_6^-$ ,  $BF_4^-$ ,  $(CF_3-SO_2)_2N^-$ ,  $ClO_4^-$ ,  $CF_3SO_3^-$ ,  $NO_3^-$  or  $CF_3CO_2^-$ . The reaction is carried out in a solvent selected typically from  $CH_2Cl_2$ , THF or  $CH_3CN$  at a temperature of from 50 to 80 °C, preferably of about  
 10 60 °C and for a period of time of from 6 to 48 hours, preferably of from 16 to 24 hours.

- The mixing with the complex is then carried out as previously leading to an ion pair representing a supported catalytic component of formula VII if the ionic liquid  
 15 is N-alkyl-imidazolium



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or of formula VIII if the ionic liquid is pyridinium



(VIII)

- 5 The present invention also discloses a catalytic component heterogenised by an ionic liquid, obtainable by the method described here -above.

An active catalyst system heterogenised by an ionic liquid is then obtained by addition of an activating agent.

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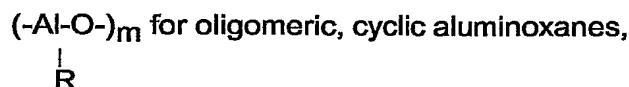
The activating agent can be selected from aluminoxanes or aluminium alkyls or boron-based activating agents.

- The aluminium alkyls are of the formula  $AlR_x$  and can be used wherein each R is the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable aluminium alkyls are dialkylaluminum chlorides, the most preferred being diethylaluminum chloride ( $Et_2AlCl$ ).

- 20 The preferred aluminoxanes comprise oligomeric linear and/or cyclic alkyl aluminoxanes represented by the formula :



25 and



wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C<sub>1</sub>-C<sub>8</sub> alkyl group and preferably methyl.

Methylaluminoxane (MAO) is preferably used.

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Suitable boron-based activating agents may comprise triphenylcarbenium boronate such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium  $[\text{C}(\text{Ph})_3^+ \text{B}(\text{C}_6\text{F}_5)_4^-]$  as described in EP-A-0,427,696

10 Other suitable boron-containing activating agents are described in EP-A-0,277,004.

The amount of activating agent is such that the Al/M ratio is of from 100 to 1000.

15 The present invention further provides a method for homopolymerising or for copolymerising alpha-olefins that comprises the steps of:

- a) injecting an apolar solvent into the reactor, then the catalytic component heterogenised by an ionic liquid and activated by a activating agent;
- b) injecting the monomer and optional comonomer into the reactor;
- c) maintaining under polymerisation conditions;
- 20 d) retrieving the polymer under the form of particles.

The conditions of temperature and pressure for the polymerisation process are not particularly limited.

25 The pressure in the reactor can vary from 0.5 to 50 bars, preferably from 1 to 20 bars and most preferably from 4 to 10 bars.

The polymerisation temperature can range from 10 to 100 °C, preferably from 20 to 70 °C and most preferably at room temperature (about 25 °C).

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The solvent is apolar and is typically selected from an alkane, preferably n - heptane.

The reaction is carried out for a period of time of from 30 minutes to 24 hours.

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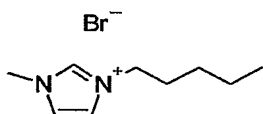
The monomers that can be used in the present invention are alpha -olefins having from 2 to 8 carbon atoms, preferably ethylene and propylene.

### Examples.

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#### Synthesis of heterogenised catalyst components using different ionic liquids.

##### Synthesis of 1-methyl-3-pentylimidazolium bromide (IL1)III).



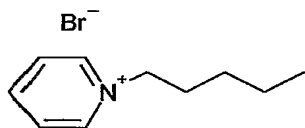
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9.96 mL of N-methylimidazole (125 mmole) were introduced in a Schlenk followed by 22.16 mL of bromopentane (187.5 mmoles). The reaction medium was stirred during 2 hours at a temperature of 90 °C. After cooling down to room temperature, 40 mL of diethyl ether were added, to form a white precipitate. After filtration, the precipitate was washed 4 times with 40 mL of diethyl ether. After filtration, 24.7 g of a white solid were obtained with a yield of 85 %.

The NMR spectra were as follows:

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 10.23 ( s, 1), 7.63 ( tr, 1), 7.47 ( tr, 1), 4.27 ( tr, 2), 1.86 ( q, 2), 1.29 ( m, 4), 0.82 ( tr, 3).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 137.17, 123.77, 122.09, 50.01, 36.67, 29.92, 28.17, 21.98, 13.76.

Synthesis of N-pentylpyridinium bromide (IL2) (IV):

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0.4 mL of pyridine (5 mmoles) were introduced in a Schlenk followed by 0.8 mL of bromopentane (7.5 mmoles). The reaction medium was stirred during 2 hours at a temperature of 100 °C until formation of a precipitate. After cooling down to room temperature, the precipitate was washed 3 times with 5 mL of diethyl ether. After

10 filtration and drying under reduced pressure, 1.09 g of a cream -coloured solid were obtained with a yield of 95 %.

The NMR spectra were as follows:

15 **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ: 9.58 ( d, 2), 8.52 ( tr, 1), 8.11 ( tr, 2), 4.93 ( tr, 2), 1.98 ( q, 2), 1.28 ( m, 4), 0.77 ( tr, 3).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ: 145.18, 128.47, 61.80, 31.66, 27.92, 22.02, 13.75.

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Synthesis of the system catalyst component/ionic liquid.

One micromole of the metallocene catalyst component ethylene bis -

25 tetrahydroindenyl zirconium dichloride (THI) was dissolved in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> to which was added one micromole of the ionic liquid dissolved in 1 mL of the same solvent. The reaction medium was kept under stirring at room temperature (about 25 °C) for a period of time of one hour. The solvent was then eliminated under reduced pressure. A yellow oil was obtained. 60 mL of n -heptane were added to

30 allow the formation of a yellow precipitate that could easily be injected into the reaction zone (The n-heptane phase was colourless).

Polymerisation of propylene.Example 1

The polymerisation conditions were as follows:

- 5        - 1  $\mu$ mole of catalyst component ethylene bis -tetrahydroindenyl zirconium dichloride (THI) and 1  $\mu$ mole of ionic liquid were mixed with 1000 equivalents of methylaluminoxane (MAO)
- 60 mL of n-heptane were added to allow the formation of a yellow precipitate that could easily be injected into the reaction zone (The n -
- 10        heptane phase was colourless).
- propylene was injected into the reactor and the system was maintained at a temperature of 70 °C and under a pressure of 5 bars during a period of time of one hour.
- the solvent was then eliminated and the residue was treated with 100 mL
- 15        of acid methanol (10 vol% HCl), then washed with water and dried under vacuum.

Example 2

- 20        The polymerisation conditions of example 1 were repeated with 1  $\mu$ mole of catalyst component  $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-Ind})_2\text{ZrCl}_2$  (cata 2) except that for the washing step 200 mL of acid methanol were used because a larger amount of polymer was obtained.
- 25        As reference example, the same amount of THI was activated with the same amount of MAO, but no ionic liquid was used.

The ionic liquids were respectively 1 -methyl-3-pentylimidazolium bromide (IL1) and N-pentylpyridinium bromide (IL2)

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The results are summarised in Table I.

**TABLE I.**

Catalytic system	Mass of polymer (g)	C <sub>3</sub> H <sub>6</sub> consumption (tons C <sub>3</sub> H <sub>6</sub> /mol/h)	Tf (°C)
THI	4.47	4.6	
THI + 1 equ. IL1	3.85	4.9	
THI + 1 equ. IL2	4.52	4.9	
cata 2	20.1	14.3	156.7
cata 2 + 1 equ. IL1	19.6	13.6	154.6

- 5 As can be seen from Table I, the presence of the ionic liquid leads to a similar catalyst activity. The polymers obtained with the ionic liquid system had substantially the same structure and the same fusion temperature as those obtained with conventional metallocene catalyst systems. In addition, the use of ionic liquids allows the preparation of a powder in n -heptane that is easily injected
- 10 into the reactor.